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1 274 635

(11) (A) No.

(45) ISSUED 900925

See to carry to 208606733

(52) CLASS 400-2024

(51) INT. CL. COBF 277/00, 279/00

(19) (CA) **CANADIAN PATENT** (12)

(54) Reinforced Weatherable Thermoplastic Manufacturing
Process

(72) Tien, Li C.;
Brubaker, Joseph D.;
Harwood, Daniel D.,
U. S. A.

(73) Granted to Dow Chemical Company (The)
U. S. A.

(21) APPLICATION No. 508,380

(22) FILED 860505

(30) PRIORITY DATE (US) U. S. A. (732,014) 850506

No. OF CLAIMS 12

Canada

508380

ABSTRACT

The invention provides an improved process for preparing a weatherable rubber modified polymer or copolymer. Rubber modified copolymers of a vinyl aromatic monomer and optionally a copolymerizable polar comonomer are prepared in a continuous, recirculated reactor process at a recirculation ratio in the range from 3 to 60.

[B]

REINFORCED WEATHERABLE THERMOPLASTIC
MANUFACTURING PROCESS

The present invention relates to a process for preparing reinforced thermoplastic resins. More 5 particularly, the present invention relates to a unique process particularly adapted to preparation of grafted amorphous olefin rubber, chlorinated polyethylene rubber or other ultraviolet light stabilized rubber modified polymers or copolymers. According to the 10 invention, a new process is employed using a recirculated reactor design to achieve essentially steady conversion during the polymerization of reinforced thermoplastics of the above general description.

In U.S. Patent 3,671,608 there is disclosed a 15 process for preparing a plastic composition, more particularly, EPDM rubber modified plastic. According to the reference, an improved product is prepared by combining an elastomer of ethylene, propylene and a nonconjugated diene (EPDM), an alkenyl aromatic monomer, 20 an acrylic monomer, an organic solvent and a free

radical initiator in a reactor operating under conditions so as to provide for the presence of at least 15 percent conversion of the monomers. This partially reacted mixture acts as a seed mixture and must be 5 present in order to prepare a rubber modified plastic having superior mechanical properties. During the polymerization, stirring is employed in order to provide thorough mixing of the seed mixture with the monomers to be polymerized. In a continuous embodiment 10 of the process, a portion of the reaction mixture is allowed to remain in an intermediate stage of conversion in the reactor in order to provide the seed mixture for the fresh feed.

In U.S. Patent 4,314,041 a similar process 15 for continuously preparing EPDM modified thermoplastic resins is provided.

In U.S. Patent 3,660,535 a polymerization process for preparing impact polystyrene employing partial recirculation is disclosed. In the process, a 20 stratifying polymerizer is employed wherein a portion of a partially polymerized feed stream is removed from the reactor at a point subsequent to phase inversion and reintroduced into the reactor and the feed stream at a location prior to phase inversion. The amount of 25 material so recirculated could vary from 5 to several hundred percent based on the feed rate of the monomer stream to the reactor.

Despite known processes for the preparation of grafted amorphous olefin rubber or other rubber 30 modified thermoplastics characterized by extremely viscous polymerization mixtures a suitable process has, until the present time, not been developed. Numerous

problems face the skilled artisan when dealing with such a polymerization system. Generally, the rubbers employed in the present invention exhibit reduced amounts of unsaturation as compared to, for example, 5 butadiene based rubbers. Because of this fact, such rubbers are greatly desired for improved weathering characteristics. However, conversely, the relative lack of unsaturation presents difficulties in obtaining sufficient grafting in order to provide compatibility 10 with the matrix phase. In order to provide adequate grafting, relatively high levels of initiators, especially free radical generating initiators, are employed. The increased amounts of free radical initiator detrimentally cause the formation of undesirable species such as cross-linked matrix or cross-linked 15 rubber.

Furthermore, amorphous olefin rubbers and EPDM in particular are less compatible with a vinyl aromatic monomer system than are butadiene rubbers especially in 20 the presence of a polar comonomer such as acrylonitrile which greatly reduces the solubility of EPDM rubber in the monomer solution.

A further difficulty with the present monomeric system is that the reaction mixture forms a relatively 25 cohesive and viscous solution. It is desirable in the polymerization to provide agitation of the reaction mixture. Such agitation provides desirable morphology and insures phase inversion and uniformity of the resulting product. In addition, agitation results in 30 obtaining a steady conversion in the reactor and the contacting of partially converted and phase inverted polymer with incoming feed thereby achieving a superior product. However, due to the cohesive and viscous

nature of the reaction mixture, agitation of the reactor has now been discovered to be an insufficient means to mix the reactor contents in order to obtain all of these desired goals. Presently available designs 5 for reactors involving various agitator designs have proven unacceptable over a wide variety of operating conditions but particularly when the mixture becomes gelatinous and difficult to stir. A failure to produce uniformity in the reaction mixture over a wide range of 10 reaction conditions may allow localized overheating forming a nonuniform or inferior product, or the formation of undesirable byproducts. These undesirable 15 byproducts such as gels, cross-linked rubbers, high molecular weight polymers, etc., adhere not only to the reactor walls but to the agitator itself, thereby further decreasing efficiency.

It might appear at first that improved impellar designs could be employed in order to assure thorough and uniform mixing. However, it is generally 20 known that designs of various agitating devices while perhaps solving one problem or obtaining better results under certain operating conditions, generally result in loss of performance under different operating conditions. In dealing with the polymeric mixtures of the instant 25 invention, the present inventors have found that regardless of agitator design it has not been possible to obtain adequate and thorough mixing of the reaction mixture. Partially due to the previous mentioned gelatinous 30 nature of the reaction mixture, helical mixers, as are normally employed, do not tend to result in adequate and thorough mixing of the reactor contents. Consequently, polymerization involving only normally available means of agitation tend, over a period of time, to result in

accumulations inside the reactor. After operation for a period of time it has been found necessary to stop the reaction, dismantle the reactor and remove such accumulation. Whether employing physical means to

5 remove such accumulations or solvents such as cyclohexanone, the loss in reactor performance and consequent inefficiency as well as the preparation of non-uniform polymer are problems which currently confront the resin producer.

10 It would be desirable to provide an improved process for preparing a weatherable rubber modified polymer or copolymer. It would further be desirable to provide such a process which provides for improved efficiency and longer operation without the need to
15 dismantle and clean the reactors. It would further be desirable to provide an improved process providing for greater uniformity of the product. It is to the obtainment of these desirable ends that the present invention is directed.

20 According to the present invention, there is provided a continuous process for the preparation of a rubber modified vinyl aromatic polymer wherein a polymerization mixture consisting essentially of a rubber selected from the group consisting of copolymers of ethylene
25 and at least one other alpha monoolefin having from 3 to 6 carbon atoms; terpolymers of ethylene and at least one alpha monoolefin having 3 to 16 carbon atoms and a diene; chlorinated polyethylene; and acrylate rubbers, vinyl aromatic monomer, and optionally a copolymerizable
30 polar comonomer, aromatic solvent and initiator is continuously charged in one or more feed streams at a rate

R_1 to the entrance of a reactor operating under essentially steady conversion conditions, and the reaction mixture comprising at least some grafted rubber modified vinyl aromatic polymer is continuously removed
5 therefrom, characterized by removing an additional amount of the reaction mixture at a rate R_2 and reintroducing the same to the reactor at a point in close proximity to the entrance thereof, the rates R_2 and R_1 being selected so that R_2/R_1 is from 3 to 60.

10 By means of the present invention it has been found that the maintenance of essentially steady conversion conditions within such reactor by the use, for example, of stirring or other means of agitation is significantly improved. Compared to a process not
15 employing recirculation the present invention results in improved product quality and increased conversion rates.

Figure 1 discloses a single reactor with associated connecting means and pumping means according
20 to the invention.

Figure 2 discloses two reaction vessels in cooperative arrangement according to the invention.

Figure 3 discloses two reaction vessels in cooperative arrangement according to the invention
25 and an additional reactor for receipt of unrecirculated polymerization product.

Figure 4 discloses two reaction vessels in cooperative arrangement according to the invention wherein styrene and acrylonitrile are combined prior

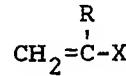
to addition or charging to the first reaction vessel in a preheating zone with mixing so as to prevent precipitation of weatherable rubber.

Vinyl aromatic monomers usefully employed according to the present invention include, by way of examples, styrene and its ring substituted derivatives such as ring halogenated or ring alkylated styrenes and alpha alkyl substituted styrenes such as alpha-methyl styrene. Mixtures of vinyl aromatic monomers may suitably be employed if desired. A preferred vinyl aromatic monomer is styrene.

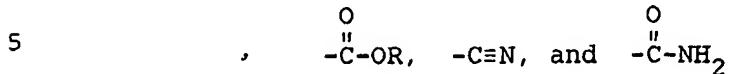
A comonomer is optionally additionally present. Because the advantages of the present process are most noteworthy in a comonomeric system, it is preferred that a copolymerizable polar comonomer is additionally present in the process. However, it will be appreciated that many advantages in the present process will be realized regardless of whether the reaction also involves such a comonomer.

Copolymerizable polar comonomers usefully employed according to the present invention include polymerizable ethylenically unsaturated anhydrides such as maleic anhydride, and those monomers corresponding to the formula

25



wherein R is selected from the group consisting of hydrogen and alkyl having from 1 to 5 carbon atoms, and X is selected from the group consisting of



and R is as previously defined. A preferred copolymerizable polar comonomer is acrylonitrile.

The rubbers usefully employed in the present invention are elastomers that are extremely low in ethylenic unsaturation. Included are copolymers of ethylene and at least one other alpha monoolefin having from 3 to 16 carbon atoms such as propylene, isobutylene, and the like; terpolymers of ethylene and at least one other alpha monoolefin having 3 to 16 carbon atoms, and a diene, eg. EPDM rubbers; chlorinated polyethylenes (CPE); acrylate rubbers; and the like. Especially suitable rubbers are EPDM rubbers, especially amorphous terpolymers comprising ethylene, propylene and a non-conjugated diene such as dicyclo pentadiene, 1,4-hexadiene and alkenyl norbornenes. Such amorphous olefin rubbers are well known in the art having been previously described in U.S. Patents 2,933,480; 3,211,709; 3,300,450; and others. In general while such weatherable rubbers as previously described provide desired improved resistance to degradation in sunlight the rubbers are not easily compatabilized in the vinyl aromatic monomer system. More specifically such

rubbers tend to produce an extremely viscous polymerization mixture and to be difficult to graft with vinyl aromatic matrix. Until a grafted rubber composition is attained the rubber may not dissolve in the monomer 5 mixture resulting in premature separation of the rubber phase.

Several techniques may be employed in order to prevent premature separation of the rubber. In one embodiment of the invention, the vinyl aromatic monomer, 10 optional copolymerizable polar comonomer and weatherable rubber may be combined in suitable solvent and preheated to an elevated temperature sufficient to avoid precipitation of the rubber prior to charging to the reactor. Alternatively, especially where a polar comonomer which 15 results in precipitation of the rubber is to be employed the reactor may be charged first with vinyl aromatic monomer rubber and optional solvent and the copolymerizable polar comonomer added separately, preferably after steady conversion conditions are obtained.

20 One or more of the previously known initiators is employed. A choice of initiator may be determined by reaction conditions, notably the temperature. It is desirable to prevent localized over heating due to the use of initiators having extremely 25 short half lives. Suitable initiators are those known as free radical polymerization initiators. Examples include azo initiators such as azobisisobutyronitrile and organic peroxides such as benzoyl peroxide, tertiary butyl peroctoate, tertiary butyl hydroperoxide, tertiary 30 butyl perbenzoyl peroxide, 1,1-ditertiary butyl peroxy-cyclohexane, dicumyl peroxide, etc. Mixtures of one or

more initiators may be employed. In fact, in a preferred embodiment in view of the fact that the weatherable rubber employed in the present invention is only with difficulty graftable, relatively high amounts of initiator are employed according to the present invention. While the amount of initiator used will vary depending on initiator identity, solvent, solvent amount, temperature, etc., general ranges may be determined. Suitably the amount of initiator is from 100 to 5,000 parts per 10 million, based on weight of monomers and olefin rubber. Preferably from 1,000 to 2,000 parts per million are employed.

Solvents which suitably may be employed include aromatic solvents such as benzene, and alkyl 15 substituted benzenes with one or more alkyl groups containing from 1 to 4 carbon atoms such as toluene, dimethyl benzene, xylene, ethyl benzene, etc. A preferred solvent is toluene.

The reaction is preferably conducted at 20 elevated temperatures above 90°C, most preferably the reaction is conducted at a temperature above 100°C.

The invention is more conveniently explained in its various embodiments by reference to the accompanying figures. In Figure 1 the invention in its simplest 25 embodiment employs a single reaction vessel having associated connecting means and pumping means to recirculate reaction mixture from the exit to a point near the entrance of the reactor.

Another embodiment of the present invention, illustrated in Figure 2, employs two reaction vessels in cooperative arrangement to form the previously described reactor such that polymerization mixture 5 removed from the exit of a first reaction vessel is charged to the entrance of the second reaction vessel optionally with the addition of a further amount of the same or different polymerization initiator. More than two reaction vessels could also be employed. If more 10 than two reaction vessels comprise the reactor the above procedure is repeated further until all the reaction vessels are in use. After proceeding through the last reaction vessel, the polymerization mixture is again removed at the exit thereof and at least some of 15 the removed reaction mixture is recharged to the entrance of the first reaction vessel. Removal of the reaction mixture and recharging of the mixture from the last reaction vessel to the first reacton vessel may be accomplished by one or more gear pumps or other suitable positive displacement devices. Polymerization 20 product exiting from the last reaction vessel and not recirculated to the entrance of the first reaction vessel may be recovered if desired, or more preferably charged to one or more additional reactors. Such 25 additional reactors may operate with recirculation as explained in the present invention or may be operated under plug flow conditions. Figure 3 depicts this system of operation additionally showing the presence of more than one pump and optional multiple initiator 30 feed streams. In a particularly preferred design of the present invention, two reaction vessels are operated in combination as one reactor in order to provide recirculation and a third reactor of essentially

equivalent volume to each of the first two reaction vessels is operated in essentially plug flow operating conditions at elevated temperatures above those of the first two reaction vessel. Polymer removed from the 5 final reactor is recovered by devolatilization according to conventional techniques.

Because the presently designed recirculated reactor operates essentially according to a steady conversion rate it is possible to add additional 10 monomers or additional initiators to the reactor at various points throughout the reactor system. For example, in order to achieve thorough mixing of additional comonomers or of initiator it is sometimes desirable that the initiator or comonomers be charged 15 at a point of intensive mixing. Accordingly, in one embodiment of the invention also illustrated in Figure 3, monomers and initiator are added to the connecting means joining the two reaction vessels. Because such connecting means are generally of smaller cross sectional area compared to the reaction vessels themselves, more rapid dispersion of the initiators is achieved. In a further embodiment of the invention, illustrated in Figure 4, monomers may be combined prior 20 to addition or charging to the first reaction vessel in a preheating zone with mixing so as to prevent precipitation of weatherable rubber.

In a typical operation under the present invention, the recirculated reactor (comprising one or more reaction vessels) is operated under steady conversion conditions so as to provide a conversion of monomers of from 50 percent to 90 percent and a solids 30

content comprising principally grafted amorphous olefin rubber modified copolymer, from 25 percent to 50 percent. Residence times in the reaction vessels and reaction temperatures may be adjusted in order to arrive at the 5 above desired operating conditions. Preferably the reaction mixture is removed from the recirculated reactor at a conversion of from 60 to 70 percent and then charged to a final reactor operating at further elevated temperatures as illustrated in Figure 3. In 10 the final reactor a conversion of monomers of from 85 to 100 percent and a solids content of 35 to 60 percent by weight is preferably achieved. In this preferred process it is desirable to employ increased reaction temperatures in the final reactor compared to those of 15 the initial recirculated reactor. For example, suitable temperatures in the recirculated reactor may be from 95°C to 110°C while temperatures in the final reactor may be controlled in the range from 105°C to 120°C. Accordingly, initiators may be selected so as to provide 20 suitable levels of radical initiators in view of the different reaction temperatures employed. The reaction mixture exiting the final reactor is then charged to a devoltilizer operating under known devoltilizing conditions so as to remove entrained solvent 25 and unreacted monomers.

Having described the invention, the following examples are provided as further illustrations thereof and are not to be construed as limiting. Unless otherwise stated all percentages are weight percentages.

Example 1

Feed is prepared by dissolving 14.5 lbs of EPDM rubber (Royalene* 505 available from Uniroyal Corporation) in 47 lbs. of toluene and 38.5 lbs. of styrene. The Royalene 505 was understood to have a Mooney viscosity of 55, an ethylene/propylene ratio of 57:43 and 5-ethylidene-2-norbornene (ENB) content of 8.5 percent. Dissolving is done at room temperature with agitation. This EPDM solution is pumped continuously at 400 g/hr to a mixer fitted with a pin agitator and having a volume of 200 cc. To this mixer is also fed 57 g/hr of acrylonitrile. A temperature of 100°C is maintained in the mixer so that a homogeneous solution of EPDM in the toluene, styrene and acrylonitrile is produced. This homogeneous solution is continuously fed to the entrance of the first of a series of stirred tube reactors which are connected in series. The first two of the stirred tube reactors additionally operate with recirculation so as to effectively constitute a single reactor. Each of the three reactors has a volume of 1400 cc with the first having an L/D of 7 and the second and third an L/D of 3.5. To the entrance of the first stirred tube reactor is also fed a 0.6 percent solution of t-butylperoctoate in toluene. The addition rate of this free radical initiator solution is 34 g/hr. The pin type agitator is rotated at 80 rpm. The partially polymerized material is continuously removed from the exit of the first stirred tube reactor and transferred to the entrance of the second stirred tube reactor also containing a pin type agitator rotating at 80 rpm. Another addition of a 0.6 percent solution of

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t-butylperoctoate in toluene at a rate of 35 g/hr is made to the partial polymer just prior to entering the second stirred tube reactor.

[B]

Recirculation of the material in the first two stirred tube reactors is accomplished by pumping material coming from the exit of the second stirred tube reactor to a point near the entrance of the first 5 stirred tube reactor where it mixes with the incoming EPDM solution. Recirculation rates are such that the ratio of the amount of the reaction mixture entering the first stirred tube reactor to the amount of new feed entering is 10:1.

10 The solids content of the material coming from the exit of the second stirred tube reactor is 39 percent and the temperature within the first and second stirred tube reactors is kept at $105^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Partially polymerized material is continuously forwarded from the 15 exit of the second stirred tube reactor to the entrance of the third stirred tube reactor. Additional free radical initiator, 1,1-ditertiary butyl cyclohexane, in a 0.35 percent solution in toluene is added to the partially polymerized mixture at a rate of 35 g/hr 20 immediately before it enters the last reactor. The temperature in the first half of the final reactor is controlled at 122°C while that in the second half is 133°C . The pin type agitator is rotated at 12 rpm. A solution containing 25 percent mineral oil, 2.5 percent Irganox^{*} 1076 and 1.5 percent dicumylperoxide in toluene 25 is added to the partial polymer at a rate of 28 g/hr at a point 2/3 of the way between the entrance and exit of the third stirred tube reactor.

Material coming from the exit of the final 30 reactor contains 48 percent solids. The reaction mixture is forwarded to a devolatilizer consisting of a

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vacuum pot with a flat plate heater maintained at 218°C and 57mm Hg followed by a devolatilizing extruder maintained at 225°C and 57mm Hg. A die at the end of the extruder forms the devolatilized polymer into a 5 strand which is then cut into pellets by an on-line cutter.

The EPDM reinforced plastic made by this process has a compression molded notched Izod impact of 11.0 ft.lbs./in notch, tensile yield = 4500 psi, tensile 10 rupture = 4400 psi, elongation at rupture = 5.8 percent. The melt flow rate was 1.5 g/10 min at ASTM condition 230/3.8. The volume average rubber particle diameter was 0.96 micron.

Examples 2-4

15 A further group of experiments was run on the same equipment as that used in Example 1. Table 1 below summarizes the recirculation rates that were used and some of the product properties that were obtained.

20

TABLE 1

<u>Exp. No.</u>	<u>$R_2 : R_1$</u>	<u>Particle Size (microns)</u>	<u>Impact Strength (ft. lbs/in notch)</u>
2	8:1	1.11	11.4 (but variable)
3	10:1	1.48	12.3 (but variable)
25	4	20:1	12.0 (11.6-12.2)

This group of experiments demonstrates the fact that on occasion it is preferred to use a recirculation ratio of 20:1 rather than 10:1.

Examples 5-7

A further group of experiments was run, but the equipment used was a pilot plant rather than the miniplant used in Examples 1-4. Table 2 below summarizes the recirculation rates that were used and some of the product properties obtained.

TABLE 2

<u>Exp. No.</u>	<u>$R_2 : R_1$</u>	<u>Particle Size (microns)</u>	<u>Impact Strength (ft. lbs/in notch)</u>
10	5	20:1	12.8
	6	30:1	11.7
	7	20:1	12.0

This group of experiments indicated that recirculation rates as high as 30:1 can be used to make a product with reasonably uniform and high Izod impact strength.

Examples 8-20

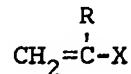
A large number of other experiments were carried out with other sources of rubber substituted for Royalene 505; and with other variations in processing conditions. Recirculation in ratios up to 58:1 were used to make a satisfactory product. However, in general, the power consumption became prohibitive at recirculation rates in excess of 50.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

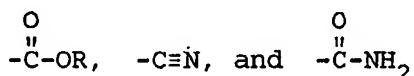
1. A continuous process for the preparation of a rubber modified vinyl aromatic polymer wherein a polymerization mixture consisting essentially of a rubber selected from the group consisting of copolymers of ethylene and at least one other alpha monoolefin having from 3 to 6 carbon atoms; terpolymers of ethylene and at least one alpha monoolefin having 3 to 16 carbon atoms and a diene; chlorinated polyethylene; and acrylate rubbers, vinyl aromatic monomer, and, if required, a copolymerizable polar comonomer, aromatic solvent and initiator is continuously charged in one or more feed streams at a rate R_1 to the entrance of a reactor operating under essentially steady conversion conditions, and the reaction mixture comprising at least some grafted rubber modified vinyl aromatic polymer is continuously removed therefrom, characterized by removing an additional amount of the reaction mixture at a rate R_2 and reintroducing the same to the reactor at a point in close proximity to the entrance thereof, the rates R_2 and R_1 being selected so that R_2/R_1 is from 3 to 60.
2. The process of Claim 1 wherein R_2/R_1 is from 3 to 50.

[B]

3. A process according to Claim 1 wherein
the copolymerizable comonomer is selected from the
group consisting of polymerizable ethylenically
unsaturated anhydrides and monomers corresponding to
5 the formula



wherein R is selected from the group consisting of
10 hydrogen and alkyl having from 1 to 5 carbon atoms, and
X is selected from the group consisting of



15 and R is as previously defined.

4. A process according to Claim 1 wherein
the rubber is an amorphous olefin rubber.

5. A process according to Claim 4 wherein
the amorphous olefin rubber is a terpolymer of eth-
20 ylene, propylene and a non-conjugated diene.

6. A process according to Claim 1, 2 or 5
wherein the vinyl aromatic monomer is styrene.

7. A process according to Claim 2 or 5
wherein the copolymerizable polar comonomer is
25 acrylonitrile.

8. A process according to Claim 1 wherein the ratio R_2/R_1 is from 10 to 30.

9. A process according to Claim 1 wherein the solvent comprises toluene, ethylbenzene or a 5 mixture thereof.

10. A process according to Claim 1 wherein the reactor comprises at least two reaction vessels in cooperative arrangement such that reaction mixture is reintroduced to the reactor by removing from the exit 10 of the first reaction vessel, charging to the second reaction vessel, removing from the exit of the second reaction vessel and charging to the first reaction vessel.

11. A process according to Claim 10 wherein 15 some of the reaction mixture removed from the exit of the second reaction vessel is charged to a third reaction vessel operating under polymerization conditions.

12. A process according to Claim 11 wherein polymer is recovered by devolatilization of the reaction 20 mixture recovered from the third reaction vessel.

Smart & Biggar
Ottawa, Canada
Patent Agents

Fig. 1

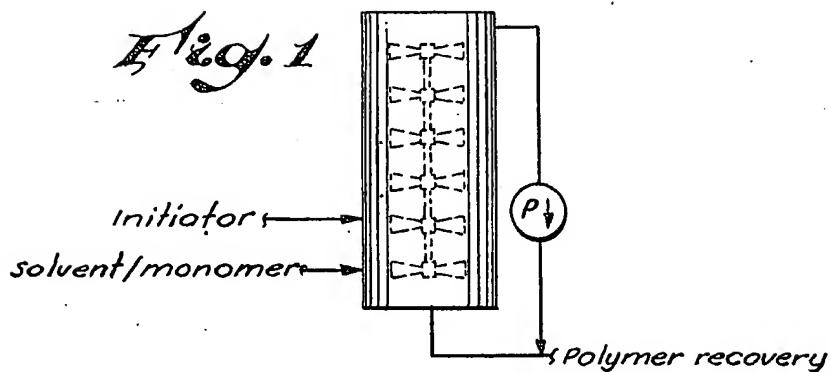
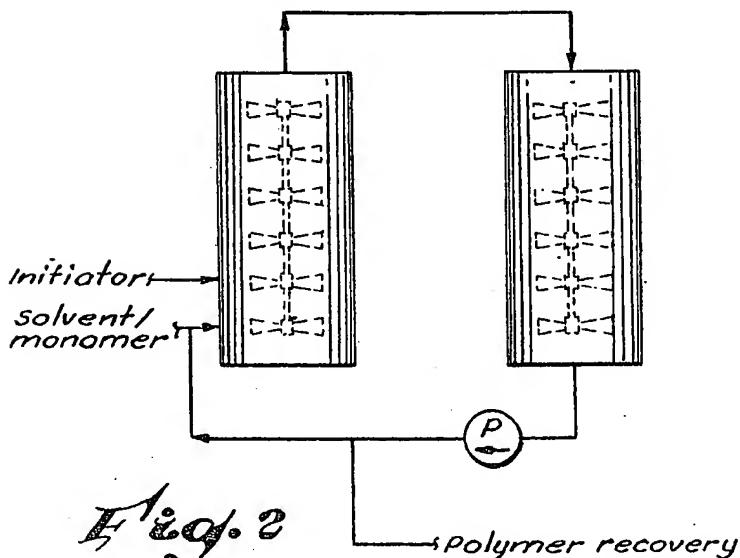


Fig. 2



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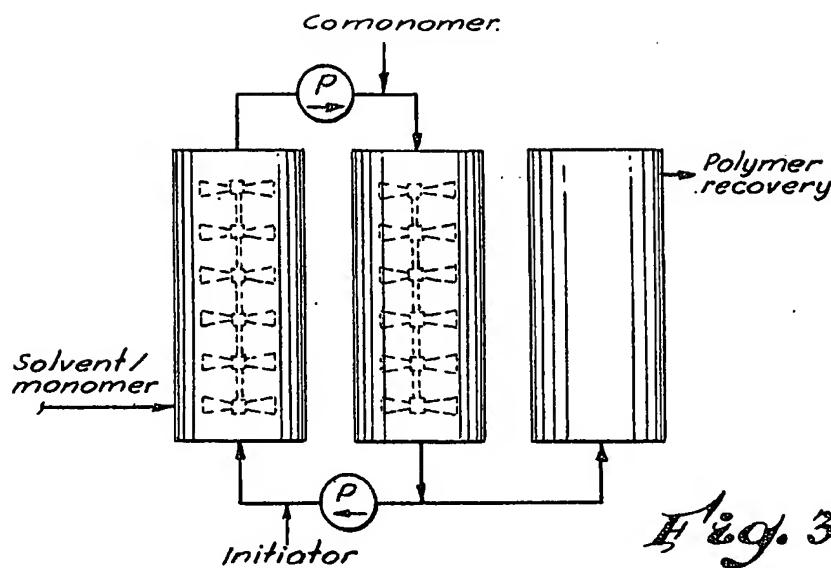


Fig. 3

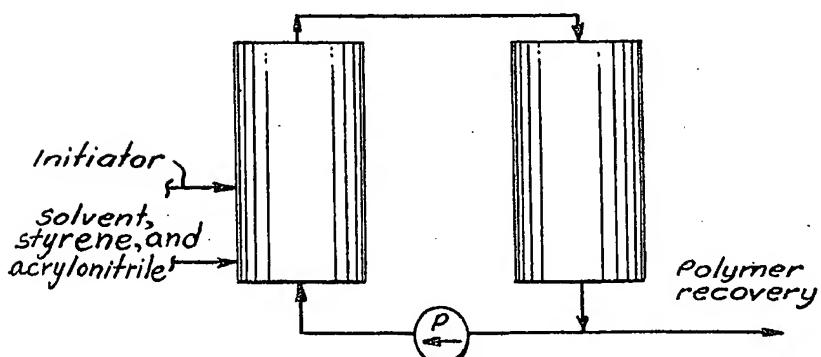
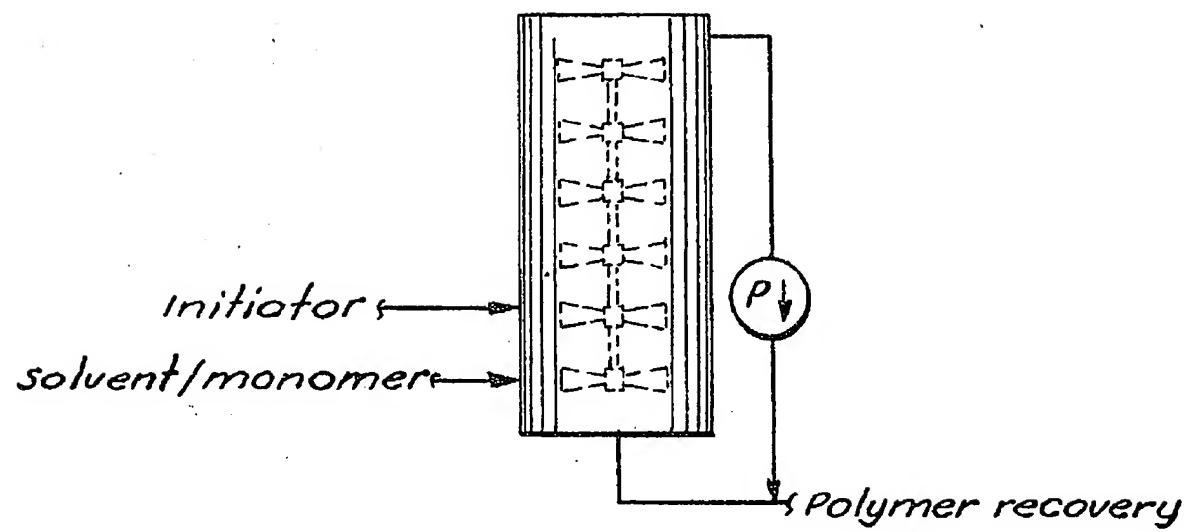


Fig. 4

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